

VIS-NIR reflectance spectra of goethite (α -FeOOH) as a function of particle size, unit-cell size, and cation substitutions. A. C. Scheinost¹ and U. Schwertmann², ¹ Purdue University, 1150 Lilly Hall of Life Sciences, West Lafayette, IN 47907, ascheinost@dept.agry.purdue.edu, ² Technische Universität München, Lehrstuhl für Bodenkunde, 85350 Freising, Germany, uschwert@pollux.edv.agrar.tu-muenchen.de.

Reflectance spectra of iron oxides and of soils containing iron oxides have bands at visible and near-IR wavelengths from crystal-field transitions of Fe^{3+} in octahedral or tetrahedral coordination. The positions of these bands has been widely used to infer the mineral composition of terrestrial and extraterrestrial soils. To evaluate the uniqueness of these inferences, however, the variability of band positions for the individual minerals has to be known. We investigated the main mechanisms responsible for the variability of band positions using goethite as a model. The results are expected to be transferable to the other iron oxides, too.

We measured the diffuse reflectance spectra (350 - 2200 nm) of 73 synthetic goethite samples with a wide variation in crystal length (TEM), mean coherence length (XRD), unit-cell size (XRD), and M-for-Fe substitution (M = Al, Co, Cr, Ni, Mn, V). The spectra were converted to absorbance and wavenumber units. The energies of the three single-electron d-d transitions, ${}^4\text{T}_{1g}$, ${}^4\text{T}_{2g}$, and (${}^4\text{E}$; ${}^4\text{A}_{1g}$), were fitted as functions of the crystal field splitting energy, 10 Dq, and the interelectronic repulsion energies, Racah B and C, assuming Gaussian energy distributions. The electron pair transition $2({}^4\text{T}_{1g})$ was fitted straight forward (Fig. 1).

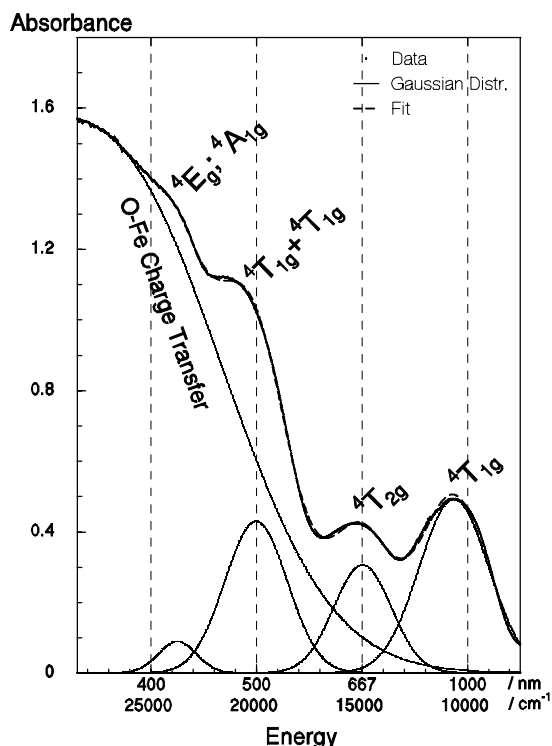


Fig. 1: Fit of the goethite spectra by Gaussian distributions.

Unsubstituted goethite with a small variation in unit-cell size showed only an insignificant variation of band positions. The total reflectance, given by the Munsell value,

varied with the particle size, revealing a maximum in light scattering for needles 1 μm in length (Fig. 2).

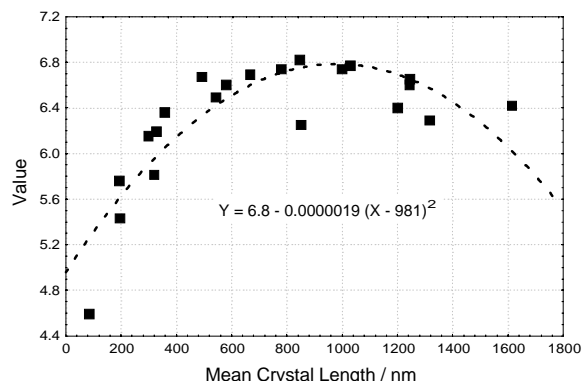


Fig. 2: Munsell value vs mean crystal length determined with TEM.

With the Al-for-Fe substitution increasing from 0 to 0.17 mole fraction, three bands shifted to lower energies: ${}^4\text{T}_{1g}$ from 10640 to 10270 cm^{-1} ($r = -0.95$) (Fig. 3, Table 1), ${}^4\text{T}_{2g}$ from 15190 to 14820 cm^{-1} ($r = -0.88$), and the electron pair transition from 20290 to 19880 cm^{-1} ($r = -0.70$). One band shifted to higher energies: (${}^4\text{E}$; ${}^4\text{A}_{1g}$) from 23630 to 24030 cm^{-1} ($r = 0.89$). The crystal field splitting energy, 10 Dq, increased from 15980 to 16720 cm^{-1} with increasing Al substitution ($r = 0.93$) (Fig. 4).

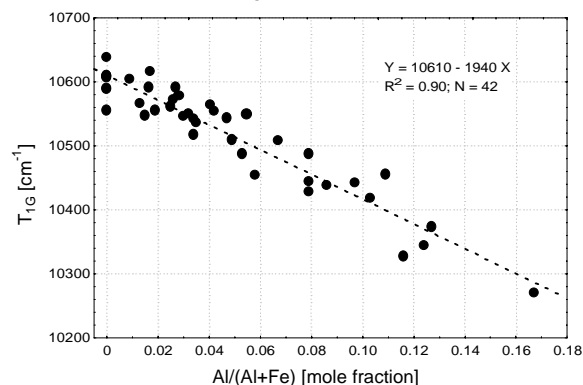


Fig. 3: Decrease of ${}^4\text{T}_{1g}$ by increasing Al substitution.

This increase of Dq can be explained by a mean decrease of the size of the octahedra caused by the smaller diameter of Al^{3+} compared to Fe^{3+} . As Al^{3+} is not susceptible to crystal field splitting, it can be assumed, that not only the octahedra occupied by Al^{3+} , but also neighboring Fe-occupied octahedra are reduced in size. As a consequence, Dq, and ${}^4\text{T}_{1g}$ and ${}^4\text{T}_{2g}$, both depending on Dq, are closely related to the unit-cell size (Table 1).

While the decrease of ${}^4\text{T}_{1g}$, ${}^4\text{T}_{2g}$ and of the electron pair transition is due to the increase of Dq, the increase of (${}^4\text{E}$; ${}^4\text{A}_{1g}$) is caused by the increase of Racah-B, indicating a

higher interelectronic repulsion of the 3d-electrons with increasing Al substitution.

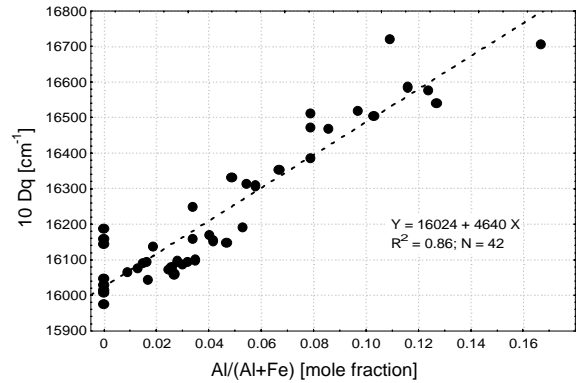


Fig. 4: Increase of the crystal field splitting energy by increasing Al substitution.

Table 1: Correlation coefficients (N = 42).

	Al subst.	UCL _a [*]	UCL _b [*]	UCL _c [*]	UCL _v [*]
⁴ T _{1g}	-0.95	0.69	0.95	0.93	0.92
⁴ T _{2g}	-0.88	0.58	0.88	0.86	0.84
2(⁴ T _{1g})	-0.70	0.64	0.70	0.68	0.71
⁴ E, ⁴ A _{1g}	0.89	-0.67	-0.89	-0.87	-0.87
Dq	0.93	-0.67	-0.93	-0.91	-0.90
Racah _C	-0.27	0.07	0.28	0.25	0.23
Racah _B	0.71	-0.47	-0.71	-0.69	-0.68

^{*}Unit-cell length in a, b, c, and unit-cell volume.

Compared to Al³⁺ the diameters of Co³⁺, Cr³⁺, Mn³⁺ and V³⁺ are much closer to that of Fe³⁺. Thus, effects of increasing substitution on unit-cell sizes and Dq are expected to be less pronounced. The transition metal cations produce, however, relatively strong, spin-allowed crystal field bands superimposed on to the weaker Fe³⁺ bands. Consequently, only a small amount of substitution changes the spectra substantially (Fig. 5). These additional bands could be separated from the Fe³⁺ bands by subtracting the spectra of the unsubstituted samples from the spectra of the substituted samples (Fig. 6). The subtracted spectra of Co-substituted goethite revealed four bands ¹T_{2g}(¹I) at 22100 cm⁻¹, ¹T_{1g}(¹I) at 17600 cm⁻¹, ³T_{2g}(³H) at 13500 cm⁻¹, and ³T_{1g}(³H) at 8100 cm⁻¹. Cr³⁺ caused at least three additional bands at 22240, 17030 and 13640 cm⁻¹; Mn³⁺ five bands at 22200, 17000, 13700, 7600 and 6500 cm⁻¹; Ni³⁺ five bands at 22430, 18170, 12850, 9730 and 7970 cm⁻¹; V³⁺ four bands at 20950, 17100, 13240 and 8120 cm⁻¹. The band assignment is still in progress.

The results indicate that cation substitutions can have a strong influence on the spectra of goethite, either by altering the crystal field of Fe-occupied octahedra and shifting the Fe³⁺-bands, or by producing additional bands between the Fe-bands and consequently concealing the characteristic Fe-bands. Similar alterations of spectra can be expected for hematite.

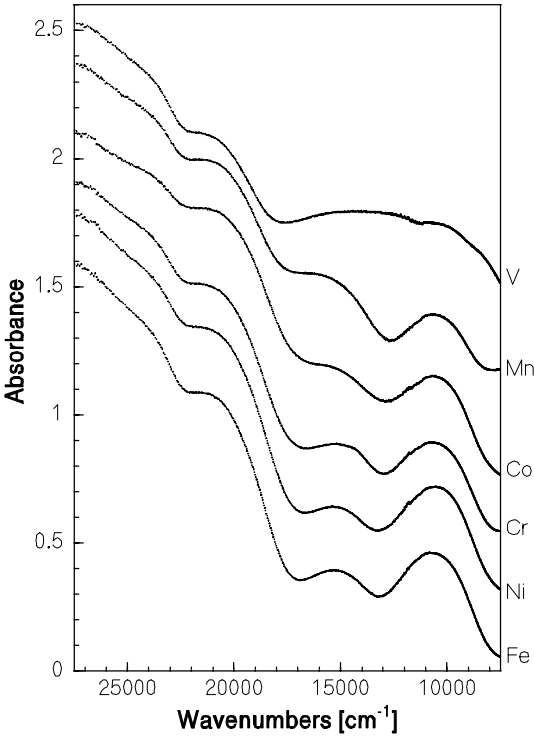


Fig. 5: Absorbance spectra (converted from reflectance spectra) of unsubstituted goethite (Fe) and of goethite substituted by 0.02 to 0.03 mole fractions of Ni, Cr, Co, Mn, and V (offset 0.2).

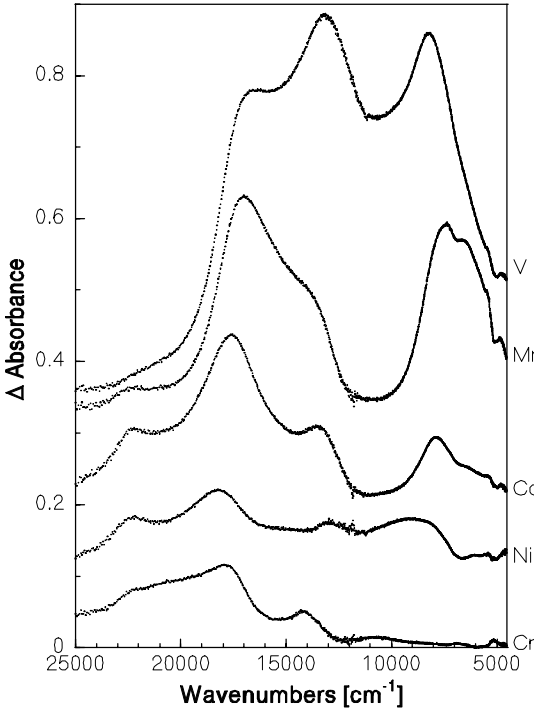


Fig. 6: Differential spectra of the absorbance spectra shown in Fig. 5 (see text, offset 0.1).